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CORRELATION BETWEEN J(^{13}C-H) IN AROMATIC METHYL COMPOUNDS AND GROUP OR ORBITAL ELECTRONEGATIVITIES

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The linear correlations of J(^{13}C-H) with group electronegativities (E_{PhY-}) and with orbital electronegativities (X_Y^V) have been presented for 11 aromatic methyl compounds (Ph-Y-CH_3) and a new correlation between J(^{13}C-H) and Gordy's effective nuclear charge ($1+n^*$) was found.

Linear correlations have been reported between J(^{13}C-H) values and atom electronegativities of the substituents in substituted methanes,$^{1)}$ ethylenes,$^{2)}$ and acetylenes.$^{3)}$

The variations in J(^{13}C-H) values have been discussed to be mainly proportional to the s-character in the C-H bond,$^{4)}$ and to depend on the effective nuclear charges of the carbon atom in halomethanes.$^{5,6)}$ Recently, Rock and Hammaker$^{7)}$ have suggested that the increase in substituent electronegativities is responsible for the increase in effective nuclear charge of the carbon 2s orbital. However, the changes in hybridization and effective nuclear charge may not really be completely separable.

In order to obtain qualitative information for these two factors, we attempted to observe the relationships between J(^{13}C-H) and the substituent group electronegativities (E_{PhY-})$^{8)}$ or orbital electronegativities (X_Y^V) in aromatic methyl compounds(Ph-Y-CH_3), because the group electronegativities have been defined as the boundary potential of effective nuclear charge acting on the valence electrons$^{9)}$ and orbital electronegativities have been found to be linearly related to the amounts of s-character in the hybride orbitals.$^{10)}$

Observed and available J(^{13}C-H) data$^{11)}$ for aromatic methyl compounds and respective electronegativities are listed in Table 1. In the calculation of group electronegativities, we used a formula analogous to that used by Wilmshurst,$^{8)}$ and used Gordy's atom electronegativities[9)] for each atom of substituents Y.

The linear plots between $J(^{13}C\text{-}H)$ and E_{PhY-} were observed indicating a trend of different slopes with periodic table variation. This trend is in qualitative

Table 1. $J(^{13}C\text{-}H)$ values(in CCl_4) for the side chain methyl groups in aromatic compounds($C_6H_5YCH_3$), group electronegativities (E_{PhY-}), and orbital electronegativities(X_Y^V).

No.	System	$J(^{13}C\text{-}H)$ (Hz)	E_{PhY-}	X_Y^V (eV)	(1+n*)	reference
1.	$C_6H_5CH_3$	125.8 126.2	2.72[a)]	17.58	5.022	11a 12
2.	$C_6H_5C(CH_3)_3$	125.5	2.50	15.95	3.961	11a
3.	$C_6H_5COCH_3$	127.1	2.56	17.58	3.644	13
4.	$C_6H_5N(CH_3)_2$	134.6 134.45	3.17	23.08	5.034	12 11a
5.	$C_6H_5OCH_3$	143.0	3.84	30.50	6.120	11a, 13
6.	$C_6H_5COOCH_3$	146.7	4.13	33.47	6.727	13
7.	$C_6H_5SCH_3$	139.2	2.58	20.27	5.973	11b, 13
8.	$C_6H_5P(CH_3)_2$	128.5	2.16	17.80	4.891	11b
9.	$C_6H_5Si(CH_3)_3$	119.2 119.5 119.1	1.77	14.59	3.801	11b 11c 12
10.	$C_6H_5As(CH_3)_2$	132.2	2.00	-	4.856	11b
11.	$C_6H_5Ge(CH_3)_3$	125.4	1.72	-	3.788	11b

a) From a least square analysis between Wilmshurst's group electronegativities $E_{X(group)}$ and $J(^{13}C\text{-}H)$ for aliphatic compounds(CH_3X) in Table 1 of the paper of Douglas,[14)] we found a linear equation as the form: $J(^{13}C\text{-}H) = 15.52\ E_{X(group)} + 83.53$. Substituting $J(^{13}C\text{-}H)$ value(=125.8 Hz) for toluene into the above empirical formula, we obtained 2.724 as the phenyl group electronegativity(E_{Ph-}).

agreement with that in the aliphatic series.[14] The results treated with Eq.(1)

$$J(^{13}C\text{-}H) = \alpha \cdot E_{PhY-} + c \qquad (1)$$

are summarized in Table 2. The linearity may substantiate qualitatively the previous conclusion.[5-7]

A linear correlation between $J(^{13}C\text{-}H)$ and orbital electronegativities (X_Y^v) of the substituent was also found with success(Eq.(2)). A trend of periodic table

$$J(^{13}C\text{-}H) = \beta \cdot X_Y^v + c' \qquad (2)$$

variation in slopes was also observed. The X_Y^v values listed in Table 1 are the orbital electronegativities for the first atom of the substituent Y bonded to methyl group, i.e., 17.58 eV for the carbon atoms of both phenyl group in toluene and carbonyl group in acetophenone, and 33.47 eV for ester oxygen of carboxyl group in methyl benzoate. The results treated with Eq.(2) are shown in Table 2. Eq.(2) may suggest that the increase in $J(^{13}C\text{-}H)$ with increasing orbital electronegativities or s-character of substituent Y is caused by an increase in p-character of the methyl carbon orbital used in bonding to the substituent and, consequently, leads to increase in the s-character of the carbon-hydrogen orbital. We also used the group orbital electronegativities of Huheey,[15] but the attempt has proved unsuccessful(r= 0.83).

We found further a new important linear relationship between $J(^{13}C\text{-}H)$ and the electronic term($1+n^*$)[8] of group electronegativities(E_{PhY-}), where n^* is the number of valence electron on atom Y in the group PhY- and ($1+n^*$) relates to the effective nuclear charge(Z_{eff}).[9] The ($1+n^*$) values are shown in Table 1. The results treated with Eq.(3) are presented in Table 2. A trend of periodic table variations in slopes was not observed. We also found that Eq.(3) is applicable to substituted methanes ($\gamma=8.43$, $c''=81.7$ Hz, $r=0.984$, $n=19$).

$$J(^{13}C\text{-}H) = \gamma\,(1+n^*) + c'' \qquad (3)$$

Recently, Yue[16] reported a linear correlation between $J(^{13}C\text{-}H)$ and the product of electronegativity and bond length($E_X \times r_{X-C}$) in 19 substituted methanes. According to Gordy's electronegativity theorem,[8] the product($E_X \times r_{X-C}$) may be qualitatively proportional to ($1+n^*$).

Table 2. The least square analysis of Eqs.(1), (2), and (3).

Eq.	Y	α,β or γ	c,c' or c''	r[a]	s[b]	n[c]
(1)	2nd period	13.25	92.1	0.993	1.222	6
	3rd period	24.58	75.7	1.000	0.316	3
	4th period	24.29	83.6	-	-	2
(2)	2nd period	1.23	105.1	0.998	0.658	6
	3rd period	3.49	67.7	0.997	1.020	3
(3)	2nd, 3rd and 4th periods	7.43	95.2	0.920	3.494	11

a) Correlation coefficients. b) Standard deviation. c) Number of compounds.

References

1) N.Muller and D.E.Prichard, J. Chem. Phys., 31, 1471 (1959).

2) a. R.E.Mayo and J.Goldstein, J. Mol. Spectr., 14, 173 (1964).
b. L.Lunazzi and F.Taddei, Spectrochim. Acta, 25A, 553 (1969).

3) L.Lunazzi, D.Macciantelli, and F.Taddei, Mol. Phys., 19, 137 (1970).

4) a. C.Juan and H.S.Gutowsky, J. Chem. Phys., 37, 2198 (1962).
b. G.E.Maciel, J.W.McIver,Jr., N.S.Ostlund, and J.A.Pople, J. Amer. Chem. Soc. 92, 1 (1970).
c. K.D.Summerhays and G.E.Maciel, Mol. Phys., 24, 913 (1972).

5) D.M.Grant and W.M.Litchman, J. Amer. Chem. Soc., 87, 3994 (1965).

6) J.E.Huheey, J. Chem. Phys., 45, 405 (1966).

7) S.L.Rock and R.M.Hammaker, Spectrochim. Acta, 27A, 1899 (1971).

8) J.K.Wilmshurst, J. Chem. Phys., 27, 1129 (1957).

9) W.Gordy, Phys. Rev., 69, 604 (1946).

10) J.Hinze and H.H.Jaffé, J. Amer. Chem. Soc., 84, 540 (1962).

11) a. C.H.Yoder, R.H.Tuck, and R.E.Hess, J. Amer. Chem. Soc., 91, 539 (1969).
b. R.E.Hess, C.K.Hass, B.A.Kaduk, C.D.Schaeffer,Jr., and C.H.Yoder, Inorg. Chim. Acta, 5, 161 (1971).
c. M.E.Freeburger and L.Spialter, J. Amer. Chem. Soc., 93, 1894 (1971).

12) N.Inamoto, S.Masuda, K.Tori, and Y.Tamura, unpublished results.

13) N.Inamoto, S.Masuda, M.Nisikida, and K.Tori, the 23rd Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1970, Abstracts III, p.1310.

14) A.W.Douglas, J. Chem. Phys., 45, 3465 (1966).

15) J.E.Huheey, J. Phys. Chem., 70, 2086 (1966).

16) C.P.Yue, Can. J. Chem., 46, 2675 (1968).

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